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VARIATIONS IN PROPERTIES OF MODIFIED GLASS USING SiO_2 BARRIER FILMS

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The results of studies account for the mechanism of the physical and chemical interaction between the ingredients of glass and barrier silica films and can be used to improve reflection parameters of glasses modified by sol-gel coatings.

Glass elements used in "cold glasses" should have the maximum possible mirror reflection coefficient in the visible spectrum range. Such elements are usually made of standard sheet glass modified with a thin film. If the film is deposited following the sol-gel technology, the solution inevitably reacts with the glass substrate, partly destroying the latter; sodium, calcium, and silicon oxides penetrate into the film and result in an undesirable decrease in its reflection coefficient. To prevent this phenomenon, SiO_2 films known as barrier films are used, which prevent the penetration of low-refractive glass components into the functional film (Japan patent application No. 58–26052) [1] and, accordingly, prevent decrease in the mirror reflection coefficient. However, the effect of the functional film compositions on the efficiency of SiO_2 barrier films is virtually not discussed in the literature, and the properties of one-coat and two-coat compositions are not correlated.

The purpose of the present study was to estimate the advisability and efficiency of using SiO_2 barrier films in production of highly reflective glass elements modified by sol-gel coatings.

The film-forming solutions (FFS) were prepared from alkoxy compounds and salts of highly reflective oxides. The silicon-bearing FFS for the barrier film contained 5% SiO_2; the total mass quantity of the film-forming oxides in the solution for the three-component iron-bearing highly reflective functional coating was equal to 2.5%. After film deposition and drying in air, the barrier film was fired at 400°C, and the functional film was fired at 450°C for 30 min. The substrate was thermally polished sheet glass 4 mm thick.

The refractive index of glass modified by films was measured ellipsometrically, the mirror reflection coefficient was measured on a Pulsar spectrocolorimeter, the Vickers microhardness was measured with a PMT-3 device, and the diffusion of sodium, calcium, and silicon from glass and their distribution at the film – substrate (glass) interface boundary was investigated using the method of secondary ionic mass spectroscopy (SIMS).

Table 1 shows the compositions of the functional films (from synthesis), and the weight content of Na_2O, CaO, and SiO_2 migrating from the substrate into the functional films in one-coat composition A and two-coat composition B. The one-coat composite is understood as a functional film deposited directly on the substrate, and the two-coat composite is a glass sample with two consecutively deposited coats: SiO_2 barrier and functional coat.

The single-coat composite has only one transitional layer, i.e., the functional film – substrate layer. The two-coat composite has two transitional layers, namely, functional film – SiO_2 barrier film and SiO_2 barrier film – glass sub-

TABLE 1

Composition	Film composition (synthesis), %*	Weight content of diffusing oxides, %			Properties of film-coated glass		
		Na_2O	CaO	SiO_2	refractive index	mirror reflection coefficient, %	Vickers microhardness, MPa
A	80 Sb_2O_3, 20 SiO_2, Fe_2O_3**	4.6	1.5	6.7	1.84	20.0	6300
B	The same	–	–	–	2.70	28.0	7140
A	80 Sb_2O_3, 20 La_2O_3, Fe_2O_3**	18.4	3.4	–	1.94	24.0	6460
B	The same	1.4	0.9	–	2.11	32.6	6930
A	30 Bi_2O_3, 70 TiO_2, Fe_2O_3**	11.3	1.5	–	2.13	34.0	6670
B	The same	1.3	0.6	–	2.15	37.0	7050

* Here and elsewhere – molar content, unless otherwise specified.

** 20% ferric oxide above 100% was added to the film.

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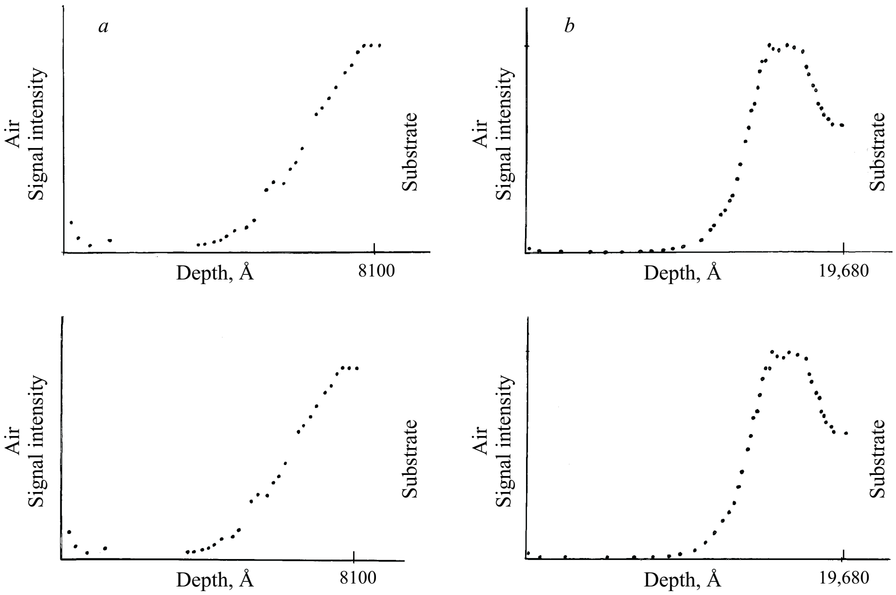

Fig. 1. SiO_2 distribution in one-coat (*a*) and two-coat (*b*) compositions.

strate. Therefore, the diffusion of glass components into the functional film in the two specified cases is not identical. Let us consider this process taking specific examples.

Functional film of the composition 80% Sb_2O_3, 20% SiO_2, plus Fe_2O_3. Figure 1 shows the silicon dioxide distribution curves of one-coat and two-coat composites. According to the SIMS data, the transition "air – substrate" layer for sodium, calcium, and silicon oxides diffusing from glass in a one-layer composition is thinner by a factor of approximately 2.5 than the same layer in the two-coat composition. The SiO_2 barrier film is 5 – 6 times thinner than the transition layer. The silica content smoothly decreases on the left and on the right of the barrier film and reaches 72.6 wt.% at the glass boundary and 4.0 wt.% at the functional film boundary (72.6 and 4.0% is the weight content of silicon dioxide in the glass and in the functional film, respectively).

The SiO_2 distribution curve in a one-coat composite rather smoothly declines from the substrate towards the film, whereas the weight content of silica varies from 72.6% in glass to 10.7% in the functional film. By comparing the latter value with the SiO_2 quantity in the coating (from synthesis), one can state that the observed increment is due to the diffusion of silicon dioxide from the glass substrate.

The semiquantitative calculations performed for the sodium and calcium distribution curves based on the method described in [2] showed that the residual weight content of CaO and Na_2O penetrating through the barrier film constitutes 0.3 and 0.5%, respectively. These insignificant quantities of low-refractive oxides are virtually totally assimilated by the "SiO_2 film – functional film" transitional layer.

The weight content of Na_2O and CaO in the functional film on the one-coat composite is regularly higher than in the two-coat composite of the same composition: 4.6 and 1.5%, respectively. Thus, in the considered case the SiO_2 barrier film completely prevents the migration of low-refractive components from the glass substrate. As a consequence, the refractive index and the mirror reflection coefficient of the glass modified by the two-layer composite is higher than that modified by the one-coat composite.

The microhardness of glass with a two-coat composite as well is higher than that of glass with a one-coat composite and is related to the observed improvement of submicrohomogeneity of the functional film (the electron microscopy method registered inhomogeneities of size 0.05 μm in the two-coat composite, against 0.50 μm in the one-coat composite). This is probably due to the chemical reactions between the film and the substrate components. In particular, the extremums on the sodium (near 4000 Å) and calcium (near 1200 Å) distribution curves corroborate this assumption. Such reactions presumably facilitate the formation of inhomogeneities that weaken the glass modified by a one-coat composite. The absence of extremums on the component distribution curves in the two-coat composite correlates with enhanced microhardness of the coated glass articles.

Functional coating of the composition 80% Sb_2O_3, 20% La_2O_3, plus Fe_2O_3. The quantity of sodium and calcium oxides diffusing from the substrate into the functional film in the one-coat composite is 4 – 15 times higher than in the two-coat composite. In general, the diffusion of components into a film of this particular composition is more intense than in the previous case. Whereas in the coating of the composition 80% Sb_2O_3, 20% SiO_2, plus Fe_2O_3, 12.8 wt.% (Na_2O + CaO + SiO_2) migrate from substrate into a one-coat composite, and 0% migrate into a two-coat composite; the same values for the film of the composition 80% Sb_2O_3, 20% La_2O_3, Fe_2O_3 are 21.8 and 2.3 wt.%, respectively. Hence it follows that the barrier effect of SiO_2 film depends on the type and the composition of the functional coating.

Similar to the first case, the properties of glass with the two-coat composite are better than with the one-coat composite: the refractive index, the mirror reflection coefficient, and microhardness are higher. This is due to the more intense migration of the low-refractive components and their probable reaction with the functional film components: the distribution extremums on the sodium and calcium distribution curves corroborate the probability of such reactions. The semiquantitative calculation points to the probability of the formation of $Na_2O \cdot Sb_2O_3$ and $CaO \cdot Fe_2O_3$ compounds in the one-coat composite. Similar calculation for the two-coat

composite cannot be implemented, due to the low concentration of the oxides migrating from the substrate.

Functional film of the composition 30% Bi_2O_3, 70% TiO_2, plus Fe_2O_3. The diffusion of sodium, calcium, and silicon oxides from the substrate into the functional film, as well as the distribution of TiO_2 (a coating component) at "the functional film – glass" boundary was studied for one-coat and two-coat compositions.

The width of the "air (functional coating) – substrate (glass)" transition layer in the two-coat composition is 1.5 times larger than in the one-coat composition, and the concentration of oxides migrating from the glass is about one-seventh of the same value in the one-coat composition.

Contrary to expectations, the maximum TiO_2 concentration in both composites was registered not near the "air – functional film" interface, but at a certain distance from this interface: about 1200 – 2200 and 4500 – 6700 Å in one-coat and two-coat composites, respectively. On the left and on the right of the specified limits, the weight content of TiO_2 decreases to 0% at the glass boundary, and to 10.7% at the boundary with air.

The variations in the considered film properties for one-coat and two-coat compositions are similar to those previously considered: the values of all parameters are higher in the two-coat composition.

Thus, a SiO_2 barrier film decreases the diffusion of oxides from the glass substrate into the functional film. The composition of the latter affects the barrier properties of a SiO_2 coating. The refractive index, mirror reflection coefficient, and Vickers microhardness of glass modified by a two-coat composition is higher than in the case of a one-coat composition.

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